Photoreaction of Methyl (*p*-Nitrophenyl)diazoacetate in the Presence of an Electron-Donating Amine: Evidence for Intermediacy of the Carbene Radical Anion

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The product distribution in the photolysis of methyl (*p*-nitrophenyl)diazoacetate in MeCN–MeOH (9:1) was dramatically changed by the addition of an electron-donating amine, where the formation of the products derived from the carbene was quenched completely. On the basis of the direct observation of transient species and the dependence of the products on amine concentration, the reaction scheme involving a single electron transfer to afford the carbene radical anion is proposed.

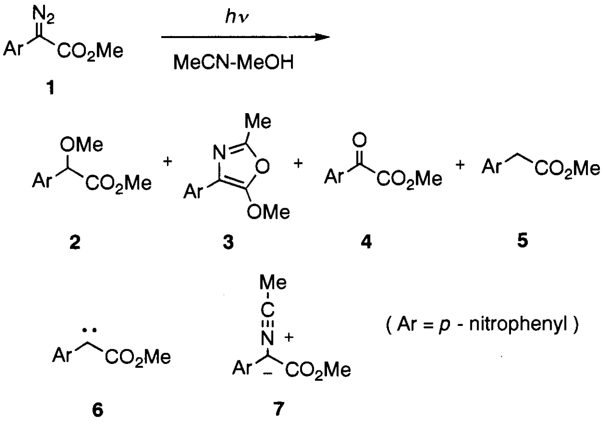
Carbene radical anions have been proposed as reactive intermediates in the cathodic reduction, as well as the reduction with sodium, of diazo compounds.[1,2] In contrast to these chemical and electrochemical approaches to carbene radical anions, however, there have been no reports on attempts to generate carbene radical anions by the use of a photoinduced electron transfer.[3] In this paper, we report the photochemistry of methyl (*p*-nitrophenyl)diazoacetate (**1**)[4] in the presence of an electron-donating amine, where we propose the mechanism involving a single electron transfer from an amine to the substrate, which affords the carbene radical anion as a reactive intermediate.

A solution of **1** in MeCN–MeOH (9:1) was purged with Ar for 5 min, and irradiated with a xenon arc lamp (> 390 nm). Separation by chromatography yielded three products, the α-methoxyacetate **2**,[4] the oxazole **3**,[5] and the glyoxylate **4**.[6] The ether **2** and the ketoester **4** are typical products obtained in the photolysis of diazo compounds, which originate from the carbene **6** in its singlet and triplet state, respectively.[7] The formation of the oxazole **3** is reasonably interpreted in terms of the intramolecular cyclization of the nitrile ylide **7**.[8] When irradiation of **1** was carried out in the presence of an amine (50 mM), the different product distributions were obtained, as shown in Table 1. Moreover, the product distribution varied with the amine employed as an additive. In the presence of TEA, methyl (*p*-nitrophenyl)acetate (**5**) was obtained instead of **4**, which seems to be explained in terms of the hydrogen abstraction of the triplet carbene from TEA to give **5** in preference to the reaction with O_2 affording **4**. However, we found that an increase in the electron-donating ability of the amine caused an increase in the yields of **4** and **5** at the expense of **2**. Especially, it was noteworthy that the formation of **2** was quenched completely in the photolysis of **1** in the presence of TMPD, which implied that a reactive intermediate other than the carbene **6** would intervene in the photoreaction processes. When the photolysis was carried out after the strict removal of O_2, no detectable amount of **4** was obtained, but the yield of **5** significantly increased instead (Table 1), indicating that the reactive intermediate generated in the presence of TMPD could afford not **2** but both **4** and **5**.[9]

Table 1. Dependence of the photoproducts on additives in the photolysis of **1** in MeCN-MeOH (9:1)[a]

Additive	E_{ox} (V vs. SCE)	Yield/%[b]			
		2	**3**	**4**	**5**
none	-	34	12	10	<1
TFDMA	1.14	27	14	10	3
TEA	1.07	38	14	<1	11
ClDMA	0.89	29	16	11	2
DMA	0.79	26	15	12	5
MeODMA	0.55	23	17	17	13
TMPD	0.12	<1	10	19	13
TMPD[c]	0.12	<1	11	<1	29

TFDMA = *p*-Trifluoromethyl-*N*,*N*-dimethylaniline, TEA = Triethylamine, ClDMA = *p*-Chloro-*N*,*N*-dimethylaniline, DMA = *N*,*N*-Dimethylaniline, MeODMA = *p*-Methoxy-*N*,*N*-dimethylaniline, TMPD = *N*,*N*,*N'*,*N'*-Tetramethyl-*p*-phenylenediamine. [a] Purged by Ar bubbling for 5 min, [**1**] = 5 mM, [Additive] = 50 mM. [b] Yield based on the reacted material (30-40%). [c] Degassed by three freeze-thaw cycles.



In order to have information about the mechanism of the photochemistry of **1** in the presence of TMPD, we tried a direct observation of transient intermediates using nanosecond laser flash photolysis technique. Irradiation of **1** (1.0 mM in MeCN) with the laser pulse (390 nm, 20 ns, 1.2 mJ/pulse) gave an intense absorption band with a maximum at 445 nm, which can be assigned to the nitrile ylide **7**.[8] On the other hand, the transient absorption spectrum recorded in the presence of TMPD (10 mM) exhibited additional bands with λ_{max} = 560 and 610 nm. The intensity of these bands increased until 300 ns after the laser pulse, and decreased slowly with a life time of > 5 μs. We assigned the transient species having these bands to

TMPD$^{+\bullet}$ by comparison with an authentic spectrum.[10] Since the diazo compound **1** is excited exclusively under the conditions of laser flash photolysis, the direct observation of TMPD$^{+\bullet}$ provides unambiguous evidence for the involvement of a single electron transfer process in the photochemistry of **1** in the presence of TMPD.

It has been proposed that a single electron transfer process is involved in the photolysis of *p*-nitrophenyl azide in the presence of an amine, though which would be suitable for the electron acceptor is still in controversy, the electronically excited azide or the nitrene.[11] Thus, our observations described above strongly suggest that the photodecomposition of **1** in the presence of TMPD in MeCN proceeds by the mechanism involving a single electron transfer from TMPD to the electronically excited diazo compound **1*** or the carbene **6**, and that the resulting diazo radical anion $\mathbf{1}^{-\bullet}$ or carbene radical anion $\mathbf{6}^{-\bullet}$ is responsible for the formation of the products **4** and **5**.

We examined the dependence of the product distribution on the TMPD concentration in the photolysis of **1**, which would provide a clue to disclosing the acceptor of electron from TMPD. As the TMPD concentration was increased from 0 to 5 mM, the yield of **2** decreased simply from 34% to 1%, while the yield of **4** increased simply from 4% to 24%.[12] Figure 1 illustrates a plot of $\Phi(\mathbf{2})^0/\Phi(\mathbf{2})$ versus [TMPD], in which $\Phi(\mathbf{2})^0$ and $\Phi(\mathbf{2})$ are the yields of **2** in the absence and in the presence of TMPD, respectively. The plot gives a curve deviating upward from a straight line predicted by a Stern–Volmer type relationship. This observation clearly implies that the reaction scheme in which a single reactive species leading to the formation of **2** is quenched by TMPD cannot be acceptable to this photoreaction. Though the detailed analysis of these data is in progress, we suppose that the nonlinear relationship shown in Figure 1 provides the evidence that both **1*** and **6** can be the acceptors of electron from TMPD.

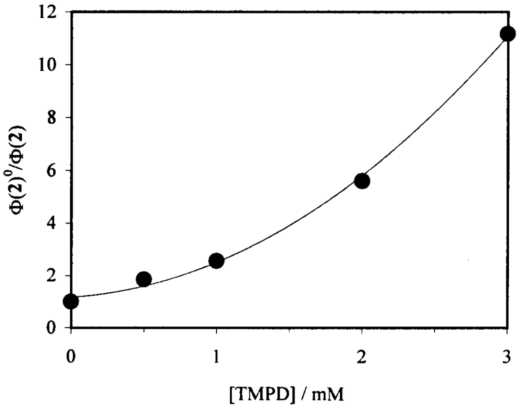
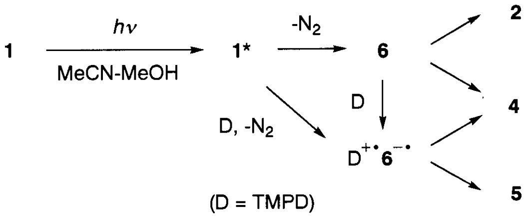


Figure 1. Dependence of the yield of **2** upon the TMPD concentration in the photolysis of **1** in MeCN-MeOH (9:1)

Assuming that **2** originates uniquely from **6**, we propose the scheme for quenching of the formation of **2** by TMPD (Scheme 1). In the presence of a high concentration of TMPD, a radical ion pair TMPD$^{+\bullet}\mathbf{6}^{-\bullet}$ would be produced not only by the direct electron transfer from TMPD to **6**, but also by the electron transfer to **1*** followed by loss of N_2. It is reasonable to think that $\mathbf{6}^{-\bullet}$ undergoes hydrogen and proton abstraction to give **5**, which is reported to be a typical reaction of carbene radical anions,[2] while the reaction with O_2 leads to the formation of **4**.



Scheme 1.

In conclusion, on the basis of the characterization of products and the direct observation of transient species, we propose that the electron transfer process to generate $\mathbf{6}^{-\bullet}$ is involved in the photoreaction of **1** in the presence of an electron-donating amine. To our knowledge, this provides the first example of the photoreaction in which a carbene radical anion intervenes as a reactive intermediate.

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References and Notes

1 T. Kauffmann and S. M. Hage, *Angew. Chem., Int. Ed. Engl.*, **2**, 156 (1963).
2 a) R. N. McDonald, F. M. Triebe, J. R. January, K. J. Borhani, and M. D. Hawley, *J. Am. Chem. Soc.*, **102**, 7867 (1980). b) D. Bethell and V. D. Parker, *J. Chem. Soc., Perkin Trans. 2*, **1982**, 841. c) D. A. V. Galen, M. P. Yound, M. D. Hawley, and R. N. McDonald, *J. Am. Chem. Soc.*, **107**, 1465 (1985). d) D. Bethell and V. D. Parker, *J. Am. Chem. Soc.*, **108**, 7194 (1986).
3 Tomioka, Tabayashi and Izawa reported that an electron transfer participated in the photolysis of *p*-nitrophenyldiazomethane in Et_2NH: H. Tomioka, K. Tabayashi, and Y. Izawa, *J. Chem. Soc., Chem. Commun.*, **1985**, 906.
4 H. Tomioka, K. Hirai, K. Tabayashi, S. Murata, Y. Izawa, S. Inagaki, and T. Okajima, *J. Am. Chem. Soc.*, **112**, 7692 (1990).
5 T. Ibata, T. Yamashita, M. Kashiuchi, S. Nakano, and H. Nakawa, *Bull. Chem. Soc. Jpn.*, **57**, 2450 (1984).
6 A. J. Muller, K. Nishiyama, G. W. Griffin, K. Ishikawa, and D. M. Gibson, *J. Org. Chem.*, **47**, 2342 (1982).
7 For reviews of reactivities of carbenes, see, for example: W. Kirmse, "Carbene Chemistry," 2nd ed., Academic Press, New York (1971).
8 Nitrile ylides are widely accepted as reactive intermediates in the photolysis of diazo compounds in MeCN, see, for example: a) P. B. Grasse, B.-E. Rrause, J. J. Zupancic, K. J. Kaufmann, and G. B. Schuster, *J. Am. Chem. Soc.*, **105** 6833 (1983). b) R. L. Barcus, L. M. Hadel, L. J. Johnston, M. S. Platz, T. G. Savino, and J. C. Scaiano, *J. Am. Chem. Soc.*, **108**, 3928 (1986). c) Y. Wang, T. Yuzawa, H. Hamaguchi, and J. P. Toscano, *J. Am. Chem. Soc.*, **121**, 2875 (1999).
9 The mechanism for the formation of the oxazole **3** in the presence of TMPD is not known at the present stage, though we suppose that **3** is at least partly formed through the reaction of **1*** with MeCN.
10 a) N. Yamamoto, Y. Nakano, and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **39**, 2603 (1966). b) S. Nakamura, N. Kanamaru, S. Nohara, H. Nakamura, Y. Saito, J. Tanaka, M. Sumitani, N. Nakashima, and K. Yoshihara, *Bull. Chem. Soc. Jpn.*, **57**, 145 (1984).
11 a) T.-Y. Liang and G. B. Schuster, *J. Am. Chem. Soc.*, **108**, 546 (1986). b) T.-Y. Liang and G. B. Schuster, *J. Am. Chem. Soc.*, **109**, 7803 (1987). c) S. Murata, Y. Mori, Y. Satoh, R. Yoshidome, and H. Tomioka, *Chem. Lett.*, **1999**, 597.
12 The yield of the oxazole **3** depended complicatedly on [TMPD]; the yield of **3** increased from 12% to 19% upon addition of TMPD (0.5 mM), and decreased gradually to 15% with increasing [TMPD] to 5 mM.